

Sorption Kinetics of Hydrophobic
Pollutants in Natural Sediments
Chapter 11

(U.S.) Environmental Research Lab.
Athens, GA

1980



U.S. Department of Commerce
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TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)		
1. REPORT NO. EPA-600/J-80-150	2. Journal Article	3 PB81-129470
4. TITLE AND SUBTITLE Sorption Kinetics of Hydrophobic Pollutants in Natural Sediments		5. REPORT DATE
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Samuel W. Karickhoff		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Research Laboratory U.S. Environmental Protection Agency College Station Road Athens GA 30613		10. PROGRAM ELEMENT NO. AIMHIE
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency--Athens GA Environmental Research Laboratory College Station Road Athens GA 30613		13. TYPE OF REPORT AND PERIOD COVERED Book article
		14. SPONSORING AGENCY CODE EPA/600/01
15. SUPPLEMENTARY NOTES In: Contaminants and Sediments, Volume 2. R.A. Baker (Ed.). Ann Arbor Science Publishers, Inc. 1980. p. 193-205. Contact: S.W. Karickhoff, 8-250-3593		
16. ABSTRACT The sorption kinetics of pyrene and phenanthrene in well-stirred sediment suspensions can be resolved into two time segments. The first is rapid (limited primarily by mixing) and presumably involves sorption to surface sites directly accessible to the bulk water phase. For this process, sorptive equilibrium can be assumed in any well-mixed sediment system. The second sorptive process involves sites accessed by a much slower mechanism. For adsorption (starting with the chemicals in the water phase), the first sorption phase is complete within 5 to 15 minutes, with the concentration of sorbed chemical achieving from 35 to 50 percent of its equilibrium value. The second sorption segment requires as much as 40 hours for the sorbed pyrene (10 hours for phenanthrene) concentration to reach 90 percent of the equilibrium value. Desorption (starting with the chemical in the sorbed state) was found to be a reversal of the adsorption process, with temporal resolution of two phases. The rate of the long-time desorptive step tended to be slightly slower than the adsorptive complement.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sorption Adsorption Desorption Pesticides Sediments Soils Solubility	Partition Coefficient Prediction of Sorption Pollutant Sorption on Sediments	02A 07C 20M 68D
19. DISTRIBUTION STATEMENT Release to Public		21. NO. OF PAGES 13
20. SECURITY CLASS (This page) Unclassified		22. PRICE

Contaminants and Sediments, Volume 2,
edited by Robert A. Baker, Ann Arbor
Science Publishers, Inc., Ann Arbor, MI
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CHAPTER 11

SORPTION KINETICS OF HYDROPHOBIC POLLUTANTS IN NATURAL SEDIMENTS

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INTRODUCTION

Most researchers have treated the sorption of organic pollutants in environmental systems as a rapid equilibrium process. In this approach, the pollutant concentration in the aqueous phase is related to the sorbed phase concentration by an equilibrium isotherm. For typical environmental pollutant concentrations, sorption isotherms in sediment suspensions approximate linearity and the aqueous phase concentration P^e (expressed relative to suspension volume*) can be related to the sorbed pollutant concentration S^e (expressed relative to dry weight sediment), by

$$S^e = K_p P^e \quad (1)$$

where K_p is the equilibrium partition coefficient for the pollutant. The aqueous phase pollutant concentration can be related to the total pollutant concentration T by

*For dilute suspensions, the volumetric water content can be assumed to be unity. That is, the suspension volume equals the aqueous phase volume.

$$p^e = \frac{T}{1 + \rho K_p} \quad (2)$$

where ρ is the sediment/water ratio.

In the investigation of pesticide mobility in soils (as mediated by sorption), nonequilibrium sorptive effects have been addressed [1,2], but no corresponding studies in suspensions have been done. However, considerable phenomenological evidence shows that retarded sorption effects in suspension can last days or even weeks. Complete recovery of sorbed chemicals by solvent extraction, for example, often requires lengthy extraction periods (days), and sorbed chemicals become increasingly difficult to extract with increased incubation time in the sorbed state. Also, sorption protocols for hydrophobic chemicals commonly specify days or weeks for equilibration.

To evaluate the significance of long-term sorptive events on pollutant fate and transport, the sorption process must be quantified kinetically. For hydrophobic pollutants in sediment suspensions, this study seeks to:

1. identify characteristic time scales for sorptive events;
2. develop phenomenological equations for sorption kinetics;
3. identify the sorbate/sorbent properties that most significantly affect sorption dynamics; and
4. formulate kinetic models for sorption processes.

Pyrene, phenanthrene and naphthalene are condensed ring hydrocarbons commonly found as environmental contaminants in geographical areas where fossil fuel combustion is widely used for energy production. Previous equilibrium sorption studies with these and similar compounds [3] revealed that for hydrophobic pollutants: (1) sorption isotherms are linear if the equilibrium aqueous phase pollutant concentration is below 1 ppm or below one half of the aqueous phase solubility (whichever is lower); and (2) sediment/water partitioning of a given chemical on different sediments is highly correlated with organic carbon content of the sediments and can generally be described by the sediment-independent K_{oc} :

$$K_{oc} = K_p/o.c. \quad (3)$$

where o.c. is the weight fraction of organic carbon in the sediment.

Kinetic studies described here for these compounds include adsorptive and desorptive approach-to-equilibrium (i.e., starting with the chemical in the water and sediment phases, respectively), and the isolation of the desorption process.

EXPERIMENTAL

Materials

Sediments used in this study were from a set of bottom sediments collected from around the U.S. and characterized by John Hassett and Wayne Banwart of the University of Illinois under an EPA contract. Table I gives a summary of sediment characterization data pertinent to this study.

Table I. Sediment Characterization

Sediment Number	Source	pH	CEC (meq/100 g)	O.C.	% Sand	% Silt	% Clay
4	Missouri River, Stanton, ND	7.8	23.7	0.021	3	55.2	41.8
6	Missouri River, Big Bend Lake, SD	7.8	33.0	0.0071	0.2	68.6	31.2
26	Mississippi River McClure, IL	7.7	20.9	0.015	1.6	42.91	55.4

Methods

Approach to Equilibrium

Adsorptive approach to equilibrium was followed by mixing aqueous solutions of a pollutant with sediment suspensions. Aliquots of the suspensions were pulled at variable times for partitioning determinations or replicate samples were initially prepared and discrete samples analyzed at variable times. In all cases, the suspended phase was separated by pressure filtration through glass microfiber filters. Sampling and phase separation required ~ 1 min. Aqueous-phase pollutant concentrations were extracted into hexane for analysis by ultraviolet (UV) absorption; sorbed pollutants were Soxhlet-extracted with hexane and analyzed by UV absorption.

Desorptive approach to equilibrium was followed by equilibrating the chemicals in concentrated sediment suspensions (slurries) and diluting the suspensions to effect desorption. Phase separation and chemical analysis was the same as that used in the adsorptive study.

Direct Solvent Extraction of Suspensions

To quantify the effect of time of pollutant incubation in sediments on recovery of sorbed pollutant via solvent extraction, aliquots of a sediment suspension (collected at various incubation times during the sorptive approach-to-equilibrium) were solvent-extracted with hexane. The suspension aliquots were shaken for 3 min with hexane and the extracted pollutant was analyzed by UV absorption.

Gaseous Purge of Suspensions

For many pollutant-sediment systems, gaseous purge of the suspensions will continuously deplete the aqueous phase pollutant and thus permit the isolation of the desorption process. Preequilibrated pollutant-sediment suspensions were purged with air (constant flowrate) and the pollutant evolution was monitored by trapping the chemicals from the purge gas on Tenax macroreticular resin. Hexane elution from the resin was performed to permit UV analysis. The time intervals for chemical collection were adjusted depending on the desired temporal resolution and the analytical sensitivity for a given chemical under the prevailing purge conditions. A publication is being prepared detailing this technique of desorption rate measurement.

RESULTS AND DISCUSSION**Kinetic Approach to Equilibrium***Adsorption*

When sediment suspensions are mixed with aqueous solutions of a pollutant, the approach to sorptive equilibrium can be resolved into two time segments. Figures 1 and 2 show the fractional approach to equilibrium of the solution phase pollutant concentration P expressed in a conventional manner; the logarithm of the quantity f

$$f \equiv \frac{P - P^e}{P^e} \quad (4)$$

is plotted versus incubation time of the pollutant in the suspension. P^e is the previously defined equilibrium solution phase concentration of pollutant. The zero time points are computed, where P_0 (P at $t=0$) is taken to be the total pollutant concentration T . Therefore, f_0 (f at $t=0$) is equal to ρK_p . All compounds displayed kinetic factoring, whereby the aqueous phase concentration decreased rapidly (5-15 min) and then approached equilibrium

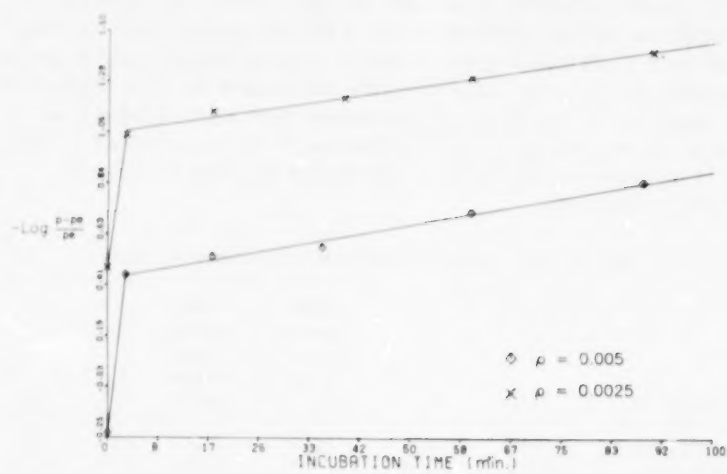


Figure 1. Phenanthrene adsorptive approach to equilibrium.

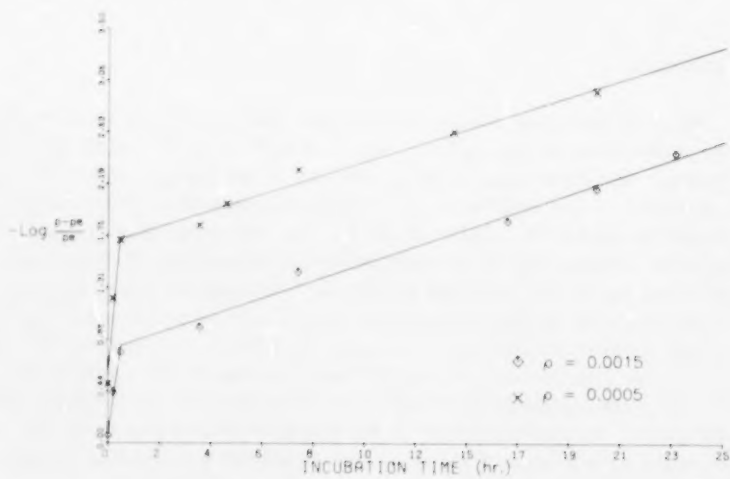


Figure 2. Pyrene adsorptive approach to equilibrium.

at a much reduced rate. Table II summarizes the time constants (i.e., slopes of the linear portions of plots of $\log f$ versus time) for the three compounds on sediment number 26. In all cases, the time constants for approach to equilibrium differed significantly (20- to 100-fold change) in the two time segments. Little attention was devoted to a precise measurement of the time constant for the "fast" segment in each case, because the times required for "completion" of this initial sorptive segment were less than the typical temporal resolution required for environmental processes. The role of sorption dynamics in environmental pollutant fate will focus on the slower sorptive component.

Table II. Time Constants for Adsorptive Approach to Equilibrium

Compound	ρ	K_p	Time Constant, Fast Process (hr ⁻¹)	Time Constant, Slow Process (hr ⁻¹)	k_d (hr ⁻¹)	X_1
Phenanthrene	0.0025	250	≥ 12	0.24	0.18	0.40
Phenanthrene	0.005	250	> 18	0.29	0.19	0.40
Pyrene	0.0005	1260	> 4	0.056	0.047	0.59
Pyrene	0.0015	1260	> 4	0.064	0.045	0.54
Naphthalene	0.05	20	> 30	1.5	1.0	0.38

Desorption

By equilibrating the chemicals in sediment slurries (where $\rho \gg 100/K_p$), the chemical can be prepared in a "highly sorbed" state. By rapidly diluting these slurries to a point at which at least half of the chemical sorbed initially is desorbed at final equilibrium, the desorptive complements of the previous studies can be achieved (Figure 3). In this case, the initial solution phase pollutant concentration P_0 is measured before dilution (i.e., P^e before dilution) and numerically corrected for dilution. Although the desorption runs characteristically showed more data scatter than the adsorptive counterparts, kinetic factoring was apparent in all cases. In addition, the approach to equilibrium (adsorption or desorption) could be described by approximately the same time constants. Mass balance problems (loss of total chemical from the system) were more prevalent in the desorptive studies because of the extended periods required for predilution equilibration plus the postdilution incubation.

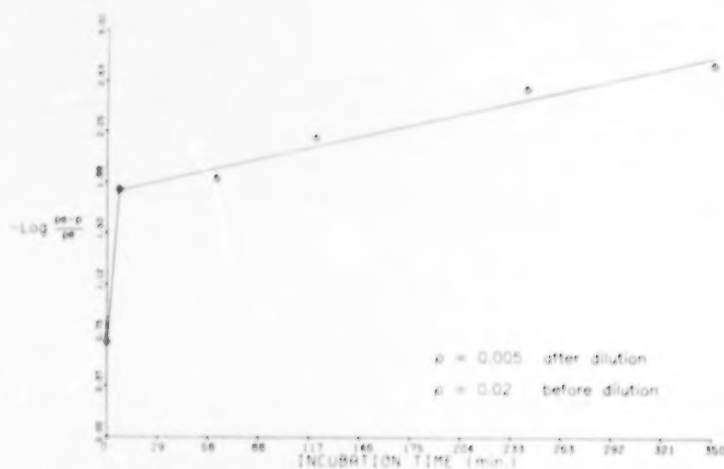


Figure 3. Phenanthrene desorptive approach to equilibrium.

Kinetic Models of Sorptive Process

A commonly used model of the sorption process describes the kinetic approach to equilibrium by first order processes in both directions.



where k_1 is a pseudo-first-order (i.e., linear in sediment concentration ρ) rate constant for the adsorptive process and k_{-1} is a first-order rate constant describing the desorptive component. For this simple model, the kinetic approach to equilibrium is given by:

$$f = f_0 \exp - (k_1 + k_{-1})t \quad (6)$$

With this model, a plot of $\log f$ versus t (e.g., Figures 1, 2 and 3) should be a single straight line with intercept $\log f_0$. However, the phenomenological behavior clearly distinguishes two segments differing considerably in temporal evolution.

This kinetic factoring can be described by a simple kinetic model that distinguishes two components:

1. A rapid component—A fraction X_1 of the total sorptive capacity is accessed by a rapid process requiring at most a few minutes for equilibration with the solution phase pollutant. Sorptive equilibrium will be assumed for this component; the concentration of pollutant sorbed by this process is denoted S_1 (referenced to total sediment mass). Although the sorption dynamics of this component can be addressed easily, the characteristic times for this component are such that equilibrium can be assumed within the typical temporal resolution of pollutant fate modeling in aquatic systems.

2. A much slower component—A fraction $(1-X_1)$ of the total sorptive capacity is accessed by a much slower process. The concentration of sorbed pollutant is denoted S_2 .



$$S_1 = X_1 K_p P \text{ for } t \geq t_1 \quad (8)$$

where k_d is a first-order rate constant for pollutant movement into and out of S_2 and t_1 is the time required for sorptive equilibration of S_1 and P .

This model describes (for $t \geq t_1$) the kinetics of interaction of the equilibrated $P + S_1$ state with the less accessible sorption state S_2 . S_1 and S_2 are distinguished only by the kinetics of transport to the water. The same partition coefficient K_p describes sorption to both states.

$$S_2^e = (1 - X_1) K_p P^e \quad (9)$$

This exchange rate of chemical between S_1 and S_2 is driven by the difference in localized concentrations.

$$\frac{d \left(\frac{S_2}{1-X_1} \right)}{dt} = k_d \left(\frac{S_1}{X_1} - \frac{S_2}{1-X_1} \right) \quad (10)$$

S_1/X_1 and $S_2/(1-X_1)$ correspond to localized concentrations within each respective sorptive state, since the concentrations S_1 and S_2 are referenced to total sediment mass. Letting k_d govern movement in both directions is equivalent to letting K_p govern equilibrium sorption to both states.

Mass balance dictates:

$$P + \rho(S_1 + S_2) = T \quad (11)$$

$$(1 + X_1 \rho K_p) \frac{dP}{dt} + \rho \frac{dS_2}{dt} = 0 \quad (12)$$

Equations 8 through 12 give an integrated form for approach to equilibrium:

$$f = f_1 \exp [-B (t-t_1)] \quad (13)$$

where f_1 is the value of f at time t_1 .

$$B = \left(\frac{1 + \rho K_p}{1 + X_1 \rho K_p} \right) k_d \quad (14)$$

Under the "adsorption" conditions described previously,

$$P_1 = \frac{T}{1 + X_1 \rho K_p} \quad \text{and} \quad f_1 = \frac{(1 - X_1) \rho K_p}{1 + X_1 \rho K_p} \quad (15)$$

The same analytic behavior as that described by Equation 13 can be obtained from a similar model in which the "slow" state S_2 is accessed directly from the solution phase by a pseudo-first-order process. When S_1 and P remain equilibrated, the "point of entry" into S_2 (i.e., directly from P or via S_1) cannot be distinguished.

By curve-fitting (least-squares linear regression), the "slow" portion ($t > t_1$) of the approach-to-equilibrium data to Equation 13 (assuming f_1 to be approximately the ordinate intercept), k_d and X_1 can be extracted (Table II). For all the compounds studied, X_1 approximates 0.5. That is, half the final equilibrium sorption is achieved in a very short period. The slower sorptive component may have characteristic times ranging from minutes to weeks depending on the compound. To a good approximation, however, k_d varies inversely as K_p for the three compounds on sediment number 26.

Direct Extraction of Sediment Suspensions

With these models, the observed kinetic factoring is brought in by subdividing the sorbed chemical into "fast" (S_1) and "slow" (S_2) configurations. Conventional sorption measurements, however, measure only the total sorbed concentration S corresponding to ($S_1 + S_2$). Direct solvent-extraction of suspensions provides a method of distinguishing sorbed configurations.

When a sediment suspension that contains a given chemical is treated directly with hexane and shaken for variable lengths of time, the amount of chemical extracted into the hexane "plateaus" after 3-5 min of shaking. That is, additional shaking results in a very slow increase in extracted chemical. The amount of chemical extracted exceeds that in the aqueous phase; some portion of the sorbed pollutant can be easily extracted.

When a sediment suspension is added to an aqueous solution of chemical (i.e., adsorption mode), the pollutant (denoted E, referenced to suspension volume) that can be extracted by a 3-min hexane extraction (from aliquots of the bulk incubating suspension) decreases with increasing pollutant incubation time in the sediments. As shown in Table III, the fraction of total pyrene extracted from a sediment suspension in the adsorption mode decreased from 0.99 after 4 min of incubation to 0.70 after 122 hr. If (in addition to direct suspension extraction) suspension aliquots are phase-separated and the aqueous phase pollutant P is determined, this can be subtracted from E to give the sorbed pollutant extracted (denoted by E_s) by direct suspension extraction. For the pyrene suspension, the fraction of sorbed pollutant extracted decreased from 0.94 after 4 min of incubation to 0.36 after 122 hr. That is, after 122 hr, the 3-min hexane extraction recovered only 36% of the sorbed pollutant.

Table III. Direct Extraction of Pyrene—Sediment (# 26) Suspension

Incubation Time	Fraction of Total Pollutant Extracted E/T	Fraction of Pollutant in Water P/T	Fraction of Sorbed Pollutant Extracted E_s/S^a	E_s/P	X_1
4 min	0.99	0.78	0.94	0.27	0.31
14 min	0.96	0.75	0.84	0.28	0.32
24 min	0.95	0.74	0.81	0.28	0.33
35 min	0.93	0.74	0.73	0.26	0.30
46 min	0.94	0.72	0.79	0.31	0.35
58 min	0.92	0.72	0.71	0.29	0.33
120 min	0.90	0.70	0.67	0.29	0.33
240 min	0.87	0.67	0.61	0.30	0.34
330 min	0.83	0.60	0.50	0.38	0.43
23 hr	0.81	0.59	0.54	0.37	0.42
29 hr	0.79	0.57	0.51	0.39	0.44
54 hr	0.76	0.55	0.47	0.38	0.43
91 hr	0.72	0.53	0.40	0.36	0.41
122 hr	0.70	0.53	0.36	0.32	0.36

^a $E_s = E - P$; $K_p = 1260$; $\rho = 0.0007$.

Interestingly, the concentration ratio of sorbed pollutant extracted (E_s) to solution phase pollutant P remains fairly constant with time. This suggests that E_s corresponds to sorbed pollutant that remains in constant equilibrium with the solution phase. Within the context of the kinetic models, E_s corresponds to ρS_1 and $E_s/p = X_1 \rho K_p$ for $t \geq t_1$. Over the

122-hr incubation period for this pyrene system, X_1 fluctuated between 0.31 and 0.44 with a mean value of 0.36. This is within the range of X_1 arrived at by curve-fitting approach-to-equilibrium data.

Similar behavior has been observed for direct extractions of phenanthrene and naphthalene suspensions.

These observations suggest that direct sediment extraction for short periods (minutes) extracts P and S_1 but S_2 requires more exhaustive extraction. In all systems studied, lengthy Soxhlet extraction (72 hr for pyrene), or sonication of the suspensions in the presence of extracting solvent recovered all of the chemical.

Gaseous Purge of Sediment Suspensions

For many hydrophobic pollutants, desorption kinetics can be followed by gaseous purge of sediment suspensions in which pollutants have been previously equilibrated. In many systems, the temporal loss of chemical from the suspension under constant purge (constant gaseous flowrate) can be factored into two rate processes: (1) the loss of chemical from the water phase (attenuated by a rapid exchange sorptive component); and (2) the release of sorbed chemical via a slower sorptive process. Figure 4 shows the loss of naphthalene from a sediment suspension, in which the

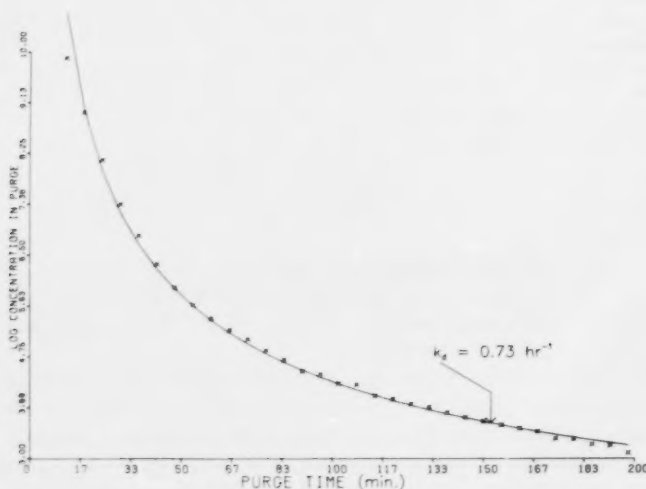


Figure 4. Gas purge of a naphthalene suspension.

two processes are distinctly resolved. The first 60 min of the purge removes the chemical from P and S_1 , clearly isolating the slower sorptive component at longer purge times. For phenanthrene and pyrene, the resolution of the two processes was not as distinct because of (1) low Henry's law constants (slower purge from solution phase) and (2) increased attenuation of the initial process because of the "fast" sorptive component. For these chemicals, the rate of purge from P and S_1 can be enhanced by diluting the suspensions just before purging, thus shifting the "fast" sorptive component toward the solution phase. Table IV gives the rate constants (corresponding to k_d) for the slower desorptive component for the three chemicals. In all cases, good agreement is found with previous determinations by approach-to-equilibrium studies (Table II). The desorption rate constants for naphthalene on the different sediments varied reciprocally with organic carbon content and, therefore, reciprocally with equilibrium K_p . This reciprocal variation of k_d with K_p seems to hold both (1) for the same compound on different sediments, or (2) for different compounds on the same sediment.

Table IV. Gaseous Purge^a Determination of Desorption k_d

Compound	Sediment Number	k_d (hr ⁻¹)
Naphthalene	4	0.49
Naphthalene	6	0.94
Naphthalene	26	0.73
Phenanthrene	26	0.14
Pyrene	26	0.031

^aPurge interval = 6 min.

SUMMARY

Dynamic approach to equilibrium (adsorptive or desorptive) in sediment suspensions reflected a factoring of the sorption process into a rapid component (S_1) and a much slower component (S_2) that may require days or weeks for complete equilibration.

The two sorbed configurations can be resolved by solvent extraction. Chemicals sorbed in the S_1 state are easily solvent-extracted, but the release of chemical from S_2 may require days for complete recovery. Thus, the recovery of sorbed pollutants by solvent extraction depends on the relative population of S_2 , or on the incubation time of the pollutant in the sediment system.

Approximately half of the total sorption sites are accessed by the fast process; this appears to hold independent of sediment or compound. Thus, approximately half of the sorptive equilibrium is realized within minutes after mixing.

For the slower process, no significant difference in rate coefficient was found between the forward and reverse reaction. The rate constants for desorption were consistently less than their adsorptive counterparts, but not significantly so (at most a factor of two).

The limited data presented reveal a reciprocal variation in k_d with K_p for (1) a given chemical on different sediments, and (2) different chemicals on the same sediment. This can be rationalized if the slower process is viewed as diffusive transfer to sorption sites that are inaccessible directly to the bulk water. Diffusive movement on a particle surface or interior to the particle (i.e., into components or in particle pores) should be mediated by sorptive steps, and thus increased sorption should result in increased impedance to diffusive transfer. An expanded data set (more chemicals and sediments) is required for an analytic description of this relationship.

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